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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C08J 5/18, B29D 7/01, C08L 23/08 // B29K 9:06, 23:00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/18263 (43) International Publication Date: 18 August 1994 (18.08.94)</p>
<p>(21) International Application Number: PCT/US94/01376 (22) International Filing Date: 3 February 1994 (03.02.94) (30) Priority Data: 08/013,518 3 February 1993 (03.02.93) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: ERDERLY, Thomas, Craig; 4114 Mohawk, Bay- town, TX 77521 (US). MACKAY, John, Hugh, III; 877 North Shore Drive, Crystal Lake, IL 60014 (US). NAR- RAMORE, Russell, Harrell; 6411 Annandale Cove, Brent- wood, TN 37027 (US). (74) Agents: MULCAHY, Robert, W. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).</p>		<p>(81) Designated States: AU, CA, CN, HU, JP, KR, PL, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: THERMOPLASTIC ELASTOMER COPOLYMER FILMS</p> <p>(57) Abstract</p> <p>Disclosed are (1) a thermoplastic elastomeric film comprised of an elastomeric arene-diene block copolymer and particular ethylene/α-olefin copolymers having low ethylene crystallinity and (2) the process of preparing films thereof. The disclosed films have superior strength and elasticity characteristics which render them particularly useful in apparel and healthcare items such as disposable diapers.</p>		

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"THERMOPLASTIC ELASTOMER COPOLYMER FILMS"

This application is a Continuation-In-Part of U.S. Application Serial No. 08/013,518, filed Feb. 3, 1993.

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FIELD OF INVENTION

This invention relates to thermoplastic elastomer blends of elastomeric block copolymers and certain olefin copolymers and, more specifically, to the fabricated films of the blends which exhibit high tensile strength and elasticity.

BACKGROUND OF THE INVENTION

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Thermoplastic elastomers are readily commercially available and are fabricated as elastomeric films in products such as disposable diapers, leggings, waistbands and gloves. Typically, these elastomeric films have been made of elastomeric block copolymers, combinations of elastomeric block copolymers and liquid butadienes, combinations of elastomeric block copolymers and ethylene vinyl acetate copolymers, thermoplastic urethanes, ethylene-propylene rubbers (EP or EPR), including ethylene-propylene diene terpolymers (EPDM), natural rubbers and combinations of polyester copolymers and ethylene-vinyl acetate copolymers. Each of these materials has suitable properties for elastomeric films, such as low tensile set, low modulus, and high elongation, but each also has acknowledged deficiencies. For example, elastomeric films containing thermoplastic urethanes, copolyesters and/or ethylene vinyl acetate copolymers are expensive due to the cost of raw materials. The tensile set and modulus of films made of these well known elastomers are acceptable for many applications, but even greater advantages would be realized from films fabricated from

elastomeric materials with lower tensile set and lower modulus.

It is well known to blend thermoplastic polymers in varying proportions with thermoplastic rubbers. Thermoplastic polymers such as polypropylene (meaning isotactic or crystalline polypropylene), polystyrene, polyethylene, ethylene-vinyl acetate copolymer, and polyurethane have been blended with thermoplastic rubber to effect compositions having varied thermoplastic and/or elastomeric properties.

The present invention relates to thermoplastic elastomer films made of elastomeric block copolymers and polyethylene/ α -olefin copolymers. The relevant prior art to same includes the following:

- A) U. S. Patent 4,476,180 describes elastomeric films comprising from about 40% to about 80% of a thermoplastic block copolymer of styrene-butadiene-styrene (S-B-S) and from about 20 to about 60% of an ethylene/vinyl acetate copolymer (EVA), the fabricated films of which demonstrate good tensile strength and elasticity. While these films demonstrate suitable properties for most elastomeric film applications, the shortcomings of these films are (1) a significantly reduced elasticity of the patented blend as compared to the elastic property of the pure elastic S-B-S copolymer; (2) difficulty in processing of the blend; and (3) typically excessive blocking of the S-B-S elastomeric copolymer. U. S. Patent 4,977,014 attempted reduction of these shortcomings by adding polystyrene to the '180 blend composition of the '180 patent.

B) Japanese patent application number 554-120646 published on September 19, 1979 discloses a composition of a styrene-butadiene elastomeric copolymer and ethylene/ α -olefin copolymer, the sole use of which composition was ineffective in film formation. This composition was rendered film-forming when a high styrenic styrene-butadiene copolymer was used as a third component. The ethylene/ α -olefin copolymer has a density of 0.87 to 0.90, and is of low crystallinity.

While all of the cited elastomeric blend film art demonstrates certain advantages relating to processability, or physical characteristics such as softness, tensile strength or elasticity, they all fail to teach or appreciate the use of elastomeric block copolymer and linear low density polyethylene ("LLDPE") blends as demonstrated in the present invention. Consequently, the prior art elastomer/polyolefin blends retain certain deficiencies relating to film fabrication for apparel or healthcare use.

As any garments or healthcare products are worn, the elastic polymers used therein must have enough elastic strength to hold any of these items snugly in place. Conversely, an unworn garment or item must have a high degree of elastic recoverability so that the elastomeric polymer used therein returns essentially to an original shape during non-use. Additionally, any elastomeric films used in apparel items must also demonstrate a high degree of repeatability as any such items are worn over a long period of time. These conditions and constraints dictate the suitability of those elastomeric compositions of the prior art which

can be fabricated into articles for garment or wear use.

As indicated above, typical elastic materials
5 utilized for clothing or healthcare applications include the thermoplastic elastomeric films of U. S. Patent 4,476,180 which contain elastomeric block copolymers of monoalkenyl arenes (styrene) and conjugated dienes (butadiene). These films generally
10 exhibit good strength and elastic properties but also undesirable excessive blocking. Blocking is the tendency of a film to adhere to itself. When films made from block copolymers of monoalkenyl arenes and conjugated dienes are stored on a roll or in stacks,
15 the film layers become difficult to unroll or unstack over a period of time due to their blocking tendency. Such blocking tendency can cause the film to tear when it is being unwound from a roll or being unstacked. To avoid such blocking it is generally necessary to add
20 significant quantities of slip and anti-block agents to the film blend. The addition of these materials is undesirable because such material can accumulate on the film fabrication apparatus, particularly the rollers, and this accumulation can result in significant down
25 time for machine cleaning.

It now has been found that the addition of certain LLDPE copolymers to elastomeric block copolymers of monoalkenyl arenes and conjugated dienes results in
30 films having substantially reduced blocking tendency while exhibiting optimum elastic properties.

BRIEF SUMMARY OF THE INVENTION

35 The instant invention is a thermoplastic elastomeric film comprising (a) from about 20% to 70%

of an elastomeric block copolymer having the general configuration:



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wherein the polymeric blocks A comprise monoalkenyl arene polymer end blocks and block B comprising an elastomeric conjugated diene polymer mid-block, the blocks A comprising from about 8 to 55% by weight of the block copolymer having a melt index of less than about 100; and (b) from about 20% to 70% of an LLDPE "plastomer" (as defined hereinafter) copolymer having less than 35% ethylene crystallinity. Particular LLDPE plastomer copolymers for use in the present blends include linear low density ethylene/ α -olefin copolymers having densities from about 0.86 to 0.90 g/cm³, molecular weight distributions of less than 6 and melt indices of between 0.2 - 1000 g/cm³.

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The LLDPE plastomer copolymers to be used in accordance with the present invention have very low ethylene crystallinity. The films made from blends of these low crystalline ethylene copolymers and elastomeric copolymers have the characteristics of high elasticity and low blocking tendency. These benefits occur because the instant film blends contain low crystalline plastomeric ethylene copolymers having certain characteristics of molecular weight distributions (Mw/Mn) (MWD), melt index (MI), density, and crystallinity.

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The films of the present invention have improved elastic recovery over those films of the prior art and provide benefits and applications where both low modulus and excellent elastic recovery are necessary as in the case of elastic components of disposable diapers. The instant films exhibit a low blocking

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tendency and consequently can be manufactured more efficiently and less expensively than other elastomeric films which require significantly more slip and anti-blocking additives for their processed blends.

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The elastomeric films of this invention are films of about .5 to 15 mils in thickness and may be produced by any well known film manufacturing processes such as these disclosed by J. H. Briston and L. L. Katan in Plastic Films, published by John Wiley & Sons, New York (2nd ed. 1983), herein incorporated by reference. Commonly known methods of producing film which may be utilized in the present invention include blowing, casting (extrusion and solvent), calendaring and extrusion methods, such as blow extrusion or slit die extrusion and cast embossed.

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Briefly, the present invention is directed to a film comprising from about 20% to 70% of a monoalkenyl arene diene elastomeric block copolymer and from about 30 to 80% of a linear low density plastomeric polyethylene (LLDPE) copolymer having a density in the range of from 0.86 to 0.90, a melt index of from .2 dg/min to 1000 dg/min, an MWD in the range of less than 6, and a CDBI greater than about 45°C.

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A process for producing the elastomeric film of this invention comprises the steps of (a) providing a thermoplastic elastomeric film blend of (1) a block copolymer elastomer and (2) an LLDPE having a density of from about 0.86 to 0.900 g/cm³, a MWD in the range of 2 to about 3.5, a melt index of less than 1000 dg/min, and an ethylene crystallinity of less than 35%; (b) extruding the blend composition through a die having a gap greater than about 5 mils and less than about 120 mils; (c) expanding the extruded film to a thickness of between 0.5 mils and about 15 mils by

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application of differential pressure as exerted by a gas and (d) rapidly cooling the expanded extruded film.

BRIEF DESCRIPTION OF THE DRAWING

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FIGURE 1 is a schematic of the present invention showing the film of the present invention being made by a blown film apparatus and process, wherein the melted thermoplastic elastomer blend is blown into a tube and
10 air cooled to form the film.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic elastomeric films of this
15 invention comprise a blend of at least two copolymers. One copolymer is an elastomeric block copolymer containing blocks of a monoalkenyl arene copolymer and a conjugated diene polymer. The second component is selected from a group of highly amorphous thermoplastic
20 ethylene copolymers having the primary characteristic of low crystallinity and low density. Optional ingredients which may also be included in the polymer blends of the present invention include small amounts of conventional anti-block concentrates and slip
25 agents.

FIGURE 1 shows a schematic of a blown film extrusion apparatus 10 and process for preparing the present film. The thermoplastic elastic pellets are
30 fed into hopper 11 of extruder 12 where the elastic pellets are heated to above their melting point. The heated and extruded material is then fed through a ring shaped die 13 where it is formed into a sleeve or tube shaped film (not shown). The tube or sleeve so formed
35 is subsequently blown and air cooled by an air ring 14 to form a bubble 15 of blown film. The bubble 15 is cooled further and then collapsed by converging frame

elements 16 and then rolled into a flattened tube 17 by nip rollers 18. The flattened film 17 is then rolled on through idle rollers 19 and 20 by take up roll 21 to form film roll 22. A slitter (not shown) is an optional station that slits film 17 into two sheets if desired.

The instant thermoplastic elastomer film blends are formulated such that they can be processed on conventional thermoplastic film making equipment such as that of Figure 1 or that used in a cast film processes. Thermoplastic elastomeric films produced with the instant blends are from about 0.5 mils to about 15 mils in thickness, preferably from about 1 to about 3 mils in thickness.

ELASTICITY

"Unload power" is the technical measure of elastic strength and an important elastic tensile property for elastomeric films to be used in garment or other skin-wear applications. For example, in diaper applications, the unload power of an elastomeric article provides indication of the retractive force which holds the elastomeric article such as a backsheet against the infant's body. In all elastomeric materials, the unload power is lower than the load power (the force required to extend the film strip). This difference shows up as a hysteresis (the differential of the force to extend and the force to hold in place) and is larger for synthetic elastomers than in the case of a natural rubber.

"Residual set" refers to the change between the length of an elastomeric material before and after its extension to a certain length for a certain time for a certain number of cycles. For example, it would be

measured by the percent change in length of a film after extension of the film to 150%, 200% and 300% of its initial length through 2.5 cycles. Each cycle would consist of extending the film beyond its initial
5 length, holding the film extending for a time period, releasing the extending force, and allowing the film to return for a time period.

THE ELASTOMERIC BLOCK COPOLYMER

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The elastomeric block copolymers contemplated for use herein are known materials having blocks of monoalkenyl arene polymer and blocks of conjugated diene polymer. The polymer blocks have the general
15 configuration:

A - B - A

and are arranged such that there are at least two monoalkenyl arene polymer end blocks A and at a least
20 one elastomeric conjugated diene mid block B. The monoalkenyl arene copolymer blocks comprised from about 8% to about 55% by weight of the block copolymer. The molecular weight of the block copolymer is such that its melt index is less than about 100 as determined by
25 ASTM Method D 1238 entitled "Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastomer" Condition E.

The term "monoalkenyl arene" includes those
30 particular compounds of the benzene series such as styrene and its analogues and homologues including o-methyl styrene and p-methyl styrene, p-tert-butyl styrene, 1,3 dimethyl styrene p-methyl styrene in other ring alkylated styrenes, particularly ring methylated
35 styrenes, and other monoalkenyl polycyclic aromatic compounds such as vinyl naphthalene, vinyl anthracene and the like. For the present invention, the preferred

monoalkenyl arenes are monovinyl, monocyclic arenes such as styrene and p-methyl styrene, styrene being particularly preferred.

5 It is critical to the present invention that the amount of monoalkenyl arene not exceed an amount of 55%, nor comprise an amount less than 8% by weight of the copolymer. Preferred amounts of monoalkenyl arene in the block copolymer are from 25% to 35%.
10 Optionally, the monoalkenyl arene will be in an amount of about 30%. If a monoalkenyl arene is used in excess of 55 weight percent, the block copolymer is too stiff for the instant blends. The elastomeric block copolymers are "oil extended" which is the addition of
15 a hydrocarbon oil and allows for improved processability and softer films. The oils are added to the commercial elastomeric copolymers in amounts of between 10% to 40%.

20 The block B comprises homopolymers of conjugated diene monomers, copolymers of two or more conjugated dienes, and copolymers of one or more of the dienes with a monoalkenyl arene as long as the blocks B are predominantly conjugated diene units. The conjugated
25 dienes preferably used herein contain from 4 to 8 carbon atoms. Examples of such suitably conjugated diene monomers include: 1,3 butadiene (butadiene); 2-methyl-1,3 butadiene; isoprene; 2,3 dimethyl-1,3 butadiene; 1,3 pentadiene (piperylene); 1,3 hexadiene
30 and the like.

For the instant films, the preferred monoalkenyl arene polymer is polystyrene; and the preferred conjugated diene polymers are polybutadiene and
35 polyisoprene, especially preferred being polybutadiene. The preferred elastomeric block copolymers are commercially available as linear tri-block copolymers

(A-B-A) from the Shell Chemical Company, Polymers Division, Houston, Texas, under the tradename KRATON and from Dexco Polymers of Houston, Texas, under the family trademark VECTOR. Especially preferred are the linear tri-block copolymers having polystyrene end blocks and a polybutadiene mid-block (S-B-S). Most commercially preferred are oil extended polymers such as KRATON D 2104 having a melt index of about 7 as determined by ASTM Method D 1238, Condition E and VECTOR 7400D, having a melt index of about 8.

The thermoplastic elastomeric films of the present invention may contain from about 20% to about 70% by weight of the elastomeric block copolymer; preferably from about 45% to about 65%; especially preferred being from about 50% to about 65%. The percentages herein are based on the total weight of the elastomeric film composition. As indicated, commercial grades of elastomeric block copolymers can be oil extended and the oil portion is not calculated as part of the percentage herein.

LINEAR LOW DENSITY PLASTOMER ALPHA-OLEFIN COPOLYMERS

As indicated above, the thermoplastic elastomeric film blends of the present invention are elastomeric block copolymers blended with amorphous linear low density ethylene/ α -olefin copolymers. The LLDPE copolymers of the instant blends are termed "PLASTOMERS". The term "PLASTOMER" as used herein refers generally to a class of ethylene based polymers with a density with less than about 0.90 g/cm³ down to about .86 g/cm³ at a weighted average molecular weight (M_w), M_w , of greater than 20,000.

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The melt index of the plastomers utilized in the invention are such that the plastomers can be extruded

into a desired end product. In the preferred embodiment, the MI must be such that the plastomer will have sufficient drawability as desired. Generally the melt index is in the range of about 0.2 dg/min to about 1000 dg/min, preferably, the MI is at least about 0.5 dg/min, more preferably at least about 1 dg/min, preferably the maximum MI is about 20 dg/min, more preferably about 5 dg/min. In another embodiment, the MI is in the range of about 0.5 dg/min to about 50 dg/min, and more preferably in the range of about 1 dg/min to about 5 dg/min. MI as measured herein was determined according to ASTM D-1238 (190/2.16). These linear low density ethylene/ α -olefin copolymers have an ethylene crystallinity between 5 to 35% and preferably between 5 to 15%. Densities were measured using ASTM D-1505 procedure, except that they were additionally conditioned by holding the resin for 48 hours at ambient temperature (23°C) prior to density measurement.

20

The plastomer utilized in the elastomeric compositions of the present invention are selected from the group of polymers consisting of ethylene copolymerized with a C₃ to C₂₀ α -olefins. The type of α -olefin comonomer selected for the plastomer herein will depend upon the type of film fabrication usage ultimately contemplated. Preferred α -olefins for use of comonomers in the plastomer polyethylene copolymers of the present film blends are C₃ to C₈ α -olefins, and the most preferred linear low density polyethylene copolymers are ethylene/propylene, ethylene/butene and ethylene/hexene copolymers.

Typically, these linear low density plastomers will generally comprise in the range of about 65 mole percent to about 93 mole percent ethylene, based on the total moles of monomer. Preferably the amount of

ethylene in these very low density copolymer plastomers ranges from about 68 to 91 mole percent. For complete effectiveness in the instant thermoplastic elastomeric film blends, the ethylene/ α -olefin copolymer plastomers preferably have an ethylene crystallinity less than about 35% and, optimally, less than about 15%. Additionally, these plastomeric copolymers have a density in the range of about 0.860 g/cm³ to about 0.90 g/cm³ and preferably, an optimum density of about 0.860 g/cm³ to .875 g/cm³.

The melt index (MI) of these plastomers is such that the plastomer can be extruded or blown into the desired film product. In addition, the MI must be such that the plastomer will have sufficient drawability as desired. Generally the melt index is in the range of about 0.2 dg/min to about 20 dg/min, preferably between 1-10, and most desirably at about 2-6 dg/min.

The plastomers utilized in this invention have a molecular weight distribution such that the polymer will have the desired drawability and be processable into the desired film end product. The ratio of M_w/M_n (polydispersity) is generally in the range of about 2 to about 6, and most preferably in the range of about 2 to about 3.

A key characteristic of the LLDPE plastomer used in the elastomeric films of the present invention is their composition distribution. As is well known to those skilled in the art, the composition distribution of a copolymer relates to the uniformity of distribution of comonomer among the molecules of the copolymer. Metallocene catalysts are known to incorporate comonomer very evenly among the polymer molecules they produce. Thus, copolymers produced from a catalyst system having a single metallocene component

hav a very narrow composition distribution - most of the polymer molecules will have roughly the same comonomer content and within each molecule the comonomer will be randomly distributed. With certain exceptions, Ziegler-Natta catalysts generally yield
5 copolymers having a considerably broader composition distribution and, consequently, comonomer inclusion will vary widely among the polymer molecules.

10 In order to achieve the molecular weight distribution ratios outlined above, it is essential that the plastomer used in the instant elastomeric blend composition be prepared from catalysts that will achieve the narrow molecular weight distribution
15 required herein. As already indicated, metallocene catalysts are highly flexible in that, by manipulation of catalyst composition and reaction conditions, they can achieve and control the molecular weight distribution of the copolymers to achieve an extremely
20 narrow molecular weight distribution or polydispersity (M_w/M_n) of about 2, to a broad distribution (as in a polydispersity of about 8). Exemplary of the development of these metallocene catalysts for the copolymerization of the ethylene and α -olefins of the
25 instant plastomers are U. S. Patent 4,937,299 to Ewen et al.; 4,808,561 to Welborn et al.; 4,814,310 to Chang et al. all the disclosures of which are hereby incorporated by reference. All of these publications describe polymerization processes using single site
30 metallocene catalysts (SSC).

Another family of catalysts which can achieve equivalent results are those Ziegler type catalysts containing vanadium halides and oxyhalides (e.g., $VC l_4$,
35 $VOCl_3$, VBr_4); and such compounds wherein at least one of valences of the metal is saturated by a heteroatom (in particular oxygen or nitrogen) bound to an organic

group, such as vanadium tribenzoylacetonate, vanadyl diacetylacetonates and the haloacetylacetonates, vanadyl trialcoholates and haloalcoholates, the tetrahydrofuranates, etherates, the aminates of
5 vanadium tri- and tetrachloride and of vanadyl trichloride, and the pyridinates and quinolinates of vanadium tri- and tetrachloride and of vanadyl trichloride. Vanadium compounds which are insoluble in hydrocarbons may also be used in preparing the
10 catalysts, particularly, the organic salts such as e.g., vanadium triacetate, tribenzoate, and tristerate.

Specific methods for making the instant ethylene/ α -olefin copolymer plastomers are taught in
15 U. S. Patent 4,871,705 to Hoel et al., hereby incorporated by reference. Utilizing single site metallocene catalysts of the cited prior art, the plastomer useful in the present elastomeric compositions can be produced in accordance with any
20 suitable polymerization process, including a slurry polymerization, a gas phase polymerization, and a high pressure polymerization process.

CDBI is a measure of composition distribution.
25 CDBI is defined as the weight percent of the copolymer molecules having a comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is
30 Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci. Poly. Phys. Ed., vol. 20, p. 441 (1982), which is incorporated herein by reference.

35 To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from TREF techniques

described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature the weight fractions less than 15,000 are ignored. These low weight fractions generally represent a trivial portion of the plastomer of the present invention. The remainder of this description and the appended claims maintain this convention of ignoring weight fractions below 15,000 in the CDBI measurements.

From the weight fraction versus composition distribution curve the CDBI is determined by establishing what weight percent of the sample has comonomer content within 25% each side of the median comonomer content. Further details of determining CDBI of a copolymer are known to those skilled in the art, see, for example, PCT Patent Application WO 93/03093, published February 18, 1993.

The composition distribution breadth index (CDBI) of the plastomers utilized in the present invention is generally about 45 percent or higher, preferably, the CDBI is about 50 percent or higher and more preferably, the CDBI is about 60 percent or higher, and most preferably, about 70 percent or higher.

The linear low density ethylene copolymers produced from the single site metallocene catalysts have been found to substantially reduce the blocking tendency of the instant elastomeric films containing them. Optimum blocking characteristics have been achieved with those elastomeric films comprising these plastomers and the styrene-butadiene-styrene copolymers sold as the VECTOR 7400 D series by Dexco Polymers.

The advantage is the use of low slip concentrations, thereby reducing cost and improving final conversion efficiency by reducing slip plate-out during lamination and by reducing the quantity of adhesive required to laminate the film to another substrate. Additionally, elastic recoverability and substantially reduced tensile set were accomplished with all metallocene engendered plastomers and elastomeric copolymer blend films compositions of the present invention when compared to the compositions taught in the prior art.

As indicated above, the EVA/elastomeric copolymer blends of U. S. patent 4,476,180 represent state of the art thermoplastic elastomeric film blend materials and are widely accepted as the most satisfactory film fabrication compositions presently available. It has now been found that permanent set of the instant plastomer/elastomeric copolymer compositions represents as much as a 60% improvement over the recovery compatibility of those ethyl vinyl acetate/elastomeric copolymer compositions taught by U. S. Patent 4,476,180.

The linear low density ethylene/ α -olefin copolymers referred to above have the characteristics of being low density and having low ethylene crystallinity giving them an amorphous crystalline structure and the physical characteristics of relatively high melt viscosity. This renders these copolymers generally miscible with the elastomeric block copolymers with which they are combined to form the film blends herein. While not to be construed as limiting, it is hypothesized that the ethylene/ α -olefin copolymers disclosed herein possess so little ethylene crystallinity that there is very little deformation set when these molecules are stretched and hence the resulting hysteresis benefits when used in

conjunction with elastomeric block copolymers to form the highly elastic films of the invention.

The amounts of plastomer in the present elastomeric films range from 20 to 60% and preferably between 25 to 50% by weight of the total composition of the film. These ranges of the plastomer component of the instant blends insure the necessary processability and elastomeric properties of these plastomer/elastomeric block copolymer film blends.

OPTIONAL INGREDIENTS

Preferred thermoplastic elastomeric films of the present invention may contain from 0 to about 4% of commercial anti-block substances preferably from about 2% to about 3.5%. Preferred anti-block substances used in films of the present invention include the silicon based masterbatch sold as CM 19002 by Quantum Chemical Company.

Reduction in blocking in the films of the present invention can also be obtained by loading the film surface with small particles of powder such as talc, chalk, clay, silica, and similar materials. Powdered polymeric materials such as polytetrafluoroethylene can also be used to reduce blocking when applied to the surface of films of the present invention. Such film treatment can be used to reduce blocking alone or in combination with other anti-block methods described herein or otherwise known in the prior art. The quantity of powder anti-block substance commonly added to the surface of a film when used is from about 0.5 g/m² to about 5 g/m².

Anti-static agents may be incorporated in films of the present invention; examples of such agents included

ethoxylated amines and quarternary amine salts having organic constituents of about 12 to 18 carbon atoms in length. Agents of this type slowly diffuse to the surface of the film and, because of their ionic
5 character, form an electrically conductive layer on the surface of the layer of the film. Anti-static agents commonly constitute from about 1% to 5% of the weight of the films, when used.

10 While anti-blocking is a central characteristic of the present film blend, small amounts of slip agents will be incorporated into the films of the present invention to further reduce drag over rollers and other forming equipment. Examples of such agents are those
15 commonly derived from amide fatty acids having from about 12 to 22 carbon atoms. Such agents may augment the superior anti-blocking properties of the films of the present invention. Such slip agents are commonly incorporated in films from about 0.05% to about 3% of
20 the weight of the films when used. Again, the present film blends are superior in anti-blocking characteristics thereby reducing the need for such slip agents, the reduction of block tendency rendering film production more efficient and less expensive.

25 In order to minimize degradation of films of the present invention during processing by extrusion or other techniques heat stabilizers and antioxidants may be added to the polymer formulations. Examples of heat
30 stabilizers that may be used are organic phosphite compounds and other organic substances such as tri-hydroxy butyrophenone. When used, heat stabilizers and antioxidants are incorporated into the polymeric formulations at levels of about 0.1% to about 2.5% by
35 weight.

Degradation of the films of the present invention by exposure to ultraviolet light can be moderated by the addition of photostabilizers. An example such photostabilizers are well known in the prior art and
5 included derivatives of benzophenone. Such photostabilizers are generally incorporated in the polymer formulations at a level from about 0.1% to about 3% when used.

10 Pigments may also be added to the polymer formulations to impart a particular color to the resulting films. Pigments are typically added to the resin blend in the form of concentrates, formulated to improved dispersion of the pigment at levels of from
15 about 0.5% to about 4% when used.

The optional constituents described here and above may be used alone or in combination with any or all of the other optional constituents in the present film
20 blends.

Film Fabrication

The invention provides a fabrication method for
25 increasing the unload power and residual set of an elastic material. According to ASTM definitions relating to rubbers, elastic materials are considered those materials which rapidly return to approximately their initial dimensions and shape after substantial
30 deformation by a weak stress and release of the stress. In the preferred embodiment, the elastic materials of the invention are considered to be those which, when stretch to one and half to twice their original length (1.5-2X) at room temperature (18°C to 29°C), and held
35 at 1.5-2X for one minute, will retract to less than 1.0X within one minute after the deforming force is released.

The present invention is directed toward an elastic film having improved unload power and residual set produced by blown, cast or embossed extrusion processes. The film is formed by any suitable method well known in the art, or once formed, the film can be subjected to a combination of post orienting and/or annealing to effect changes in its unload power. Such methods of making film are discussed by the earlier cited J. H. Briston and L. L. Katan in Plastic Films, (2nd ed. 1983) and U.S. patent Numbers 4,436,520 and 5,066,526, the disclosures of which are herein incorporated by reference. Commonly know methods of producing film include casting (extrusion and solvent), calendaring and extrusion methods, such as blow, slit extrusion or cast die extrusion, or cast embossed extrusion. A preferred preparation of the instant composition is the blown film process of Figure 1.

The invention in another embodiment is suitable for improving the unload power of thin elastic articles. Such thin elastic articles are commonly known as ribbon, tape, film, strip, sheet, and the like. The differences between these particular terms is generally dimensional. For example, tape is generally thought of as being narrower than film. For the purposes of this patent specification, the terms "ribbon", "tape", "film", "sheet", and "strip" are generally interchangeable.

Regardless of the method of first producing the film, once made, the film can be used as is, or it can be further processed to improve unload power of the film. This further processing is accomplished by a combination of orienting and/or annealing the film. In one embodiment, the annealing is conducted at a temperature between the film softening point and

melting point. Orientation of non-elastic films such as polypropylene, polystyrene, nylon and polyethylene terphthalate to improve clarity, impact strength and particularly in the case of polypropylene, its barrier properties, is well known in the art. The orienting and annealing of the film may be carried out monoaxially in the machine direction (MD) or the traverse direction (TD) or in both directions (biaxially) either simultaneously or sequentially using conventional equipment and processes following cooling of the film.

Blown films are preferably stretched in machine direction or in both directions. Cast films are preferably stretched in the machine direction. Generally, for orientation in the machine direction, the film is passed around two rollers driven at different surface speeds and finally to take up roller. The second driven roller which is closest to the take up roll is driven faster than the first driven roller. As a consequence, the film is stretched between the driven rollers. Conventional "godet" stands as are well known in the art may also be utilized.

Film orientation in another embodiment may also be carried out in a tentering device with or without machine direction orientation to impart transverse direction orientation in the film. The film is gripped by the edges for processing through the tentering device. For most final applications, the film is monoaxially oriented in the machine direction.

The morphology of the instant elastomer/plastomer films can be viewed as a matrix of amorphous material interspersed with crystallites. For orienting, it is generally necessary that the film be heated to between its softening point and its melting point. This

heating is necessary to allow extension or orientation to be induced into the film. Since the temperature is between the film softening point and melting point, the smaller imperfect crystallites will melt, whereas
5 larger more perfect crystallites of the plastomer will remain. The molecules in the amorphous matrix become oriented or extended depending on the draw ratio and other material and fabrication parameters.

10 In one embodiment, the film of the invention is annealed at a temperature between the film softening point and melting point. The annealing step is necessary to anneal or perfect the crystallites that survived the orienting step and to relax out stresses.
15 This annealing aids in maintaining the orientation or extension induced in the orienting step. The annealing temperature is preferably less than the orienting temperature. Generally once the film leaves the annealing step, ambient cooling is sufficient. In most
20 cases, the film from the annealing step is then spooled in a winding unit.

Industrial Applicability

25 The thermoplastic elastomeric films of the present invention may be used in a wide variety of applications where thin, elastic material would be useful. Such films are particularly useful as low cost elastic members for disposable wearing apparel such as diapers,
30 training pants, feminine hygiene devices, medical gowns, gathered laminate garments, non-woven head bands, sports apparel, bandages and protective clothing.

EXAMPLES

The following examples illustrate preferred embodiments of the invention in comparison to similar standard compositions not employing the plastomeric olefin copolymers illustrated in the thermoplastic elastomeric film blends of the present invention. All experiments were conducted with the materials indicated in the tables. All examples employed a styrene-butadiene elastomeric block copolymer in the commercial form of Shell's KRATON D 2104 and Dexco's VECTOR 7400D which was blended with the olefin copolymers of the present invention.

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A. COMPOSITION

The character and commercial source of the elastomeric and LLDPE copolymer resins used in the examples are listed in the following table.

TABLE I

RESIN	RESIN TYPE	MI (DG/MIN)	DENSITY (G/CM ³)	COMONOMER	SUPPLIER
KRATON D-2104	SBC	4.25	.930	SBS	SHELL
VECTOR 7400D	SBC	8.0	.930	SBS	DEXCO
LD-767	EVA	3.2	-	28% VA	EXXON
XS-12.04	EMA	3.0	-	28% MA	EXXON
TAFMER P0480	MTSUI	1.0	.867	EP	MTSUI
TAFMER P0280	MTSUI	3.0	.867	EP	MTSUI
TAFMER P0480	MTSUI	8.0	.867	EP	MTSUI
EXACT WS-9905	EXXPOL	4.1	.874	EB	EXXON
EXACT 4049	EXXPOL	4.5	.873	EB	EXXON
MBX-6	MB	8.6	1.176	SLIP = 3%	EXXON
				A/B = 35%	
				A/O = 0.2%	
				CARRIER =	
				LDPE	

The compositions employed in the following examples contain an additive package of 0.2% of IRGANOX 1076 stabilizer sold by Ciba-Geigy Corporation, 0.3% of Eucaramide Slip Crodamide ER sold by Humko Chemical and 3.5% of Superfloss Silica anti-blocking agent sold by Manville Corporation. The anti-block was introduced in the form of a 50/50 (LDPE/anti-block) masterbatch (CM 19002) supplied by Quantum Chemical Company, for hot melt blend formulations. The melt index of the film compositions or components was determined according to ASTM Method D 1238, condition E as indicated.

B. COMPOUNDING

All formulations identified in Table III, Examples 6-11, were hot melt compounded on a 57 mm twin screw ZSK Extruder manufactured by Werner Pfleiderer at melt temperatures not exceeding 350°F. The extruder has a length diameter ratio (L/D) of 24:1. Feed rates ranged from 500 to 300 lbs/hr and water temperatures ranged from 78 to 55°F. The blends of Table II were dry blended as indicated.

C. FILM FABRICATION

Film was produced on a 1 1/2 inch Egan Blown Film extruder having 24:1 L/D and a 3 inch die. The melt temperature of the film blend was about 320°F. The BUR was 2:1 and films of about 2 mil thickness resulted.

The blowup ratio of blown films is calculated as the ratio of the total lay-flat with blown film to the circumference of the inner circle of the film dye.

The blown film conditions in the Egan Line extrusion process for the two sets of samples subjected to the respective 200% and 150% extensions are outlined in Tables II and III as follows.

Two examples of films fabricated for data of Table VI were prepared on a 4 1/2 inch commercial film line at Exxon Chemical Company in Lake Zurich, Illinois.

TABLE II

BLOWN FILM EXTRUSION CONDITIONS FOR SAMPLES SUBJECTED TO 200% EXTENSION

SAMPLE ID	BUR	DIE GAP (MIL)	YAG (MIL)	EXT SPEED (RPM)	EXT. LOAD (AMPS)	EXT. PRESS (PSI)	FLH (IN)	MELT TEMP (°F)	SCREEN PACK
001 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	35	2.05	30	20	1450	9.5	320	40/120/40
002 KRATON D2104, SBC 28% EMA	2.1	35	2.37	30	22	1150	9.5	358	40/120/40
003 KRATON D2104, SBC 28% TAFMER P0480	2.1	35	2.40	30	28	2100	10	410	40/120/40
004 KRATON D2104, SBC 28% TAFMER P0280	2.1	35	2.32	30	25.5	1600	10	410	40/120/40
005 KRATON D2104, SBC 28% TAFMER P0180	2.1	35	2.19	30	26	1650	9.5	378	40/120/40

NOTE: ALL BLEND FORMULATIONS ARE DRY BLENDED WITH A SLIP, ANTIBLOCK MASTERBATCH (MBX-6).
FILM FABRICATED ON A 1 1/2", 24:1 L/D FILM EXTRUDER.

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TABLE III

BLOWN FILM EXTRUSION CONDITIONS FOR SAMPLES SUBJECTED TO 150% EXTENSION

SAMPLE ID	BUR	DIE GAP (MIL)	YAG (MIL)	EXT SPEED (RPM)	EXT. LOAD (AMPS)	EXT. PRESS (PSI)	FLH (IN)	MELT TEMP (°F)	SCREEN PACK
006 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	35	2.19	30	23	1770	9	320	20/40/80/20
007 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	50	2.89	30	22	1090	9.5	325	20/40/20
008 KRATON D2104, SBC 28% EXXPOL	2.1	35	2.31	30	29	2460	10	320	20/40/80/20
009 KRATON D2104, SBC 46% EXXPOL	2.1	35	2.25	30	32	2660	10	320	20/40/80/20
0010 VECTOR 7400D, SBC 28% EXXPOL	2.2	50	2.68	30	29	1630	12.5	327	20/40/20
0011 VECTOR 7400D, SBC 46% EXXPOL	2.2	50	2.63	30	29	1580	12.5	327	20/40/20

NOTE: ALL BLEND FORMULATIONS HOT MELT COMPOUNDED ON A TWIN SCREW EXTRUDER WITH SLIP, ANTIBLOCK MASTERBATCH. FILM FABRICATED ON A 1 1/2", 24:1 L/D FILM EXTRUDER.

D. HYSTERESIS

The ultimate tensile strength and elongation were determined according to ASTM D-882-81 Method using an INSTRON Model 1122 Tester. The tensile properties of the film were measured in the direction of extrusion of the film (machine direction, MD); and in the direction perpendicular to the direction of the extrusion (cross-machine direction, CD or traverse direction (TD)). Test specimens were cut along the direction of extrusion of the film (MD) and along the traverse direction in segments of 1 inch wide and 6 inches long.

The hysteresis testing is an Exxon variation of a procedure described by DuPont in its brochure on its polyether urethane elastic product, T-722A. In the Exxon variation, 1 inch x 6 inch strips are subjected to a strain rate of 150% or 200% or 300% with a jaw gap separation of 2" and crosshead speed of 20"/min. the hysteresis stress/strain curve is plotted on a chart also traveling a 20"/min. Both the extension and retraction crosshead speeds (20"/min.) were the same and performed on an Instron model 1123. The film was held for 60 seconds at maximum extension and then retracted and held for 30 seconds relaxation prior to the next cycle. This was repeated 2 1/2 times. Key pieces of information that are extracted from these stress/strain plots are the maximum force (modulus) of each cycle, the residual set or permanent set (the degree of deformation as measured by the point of stress divided by total strain/cycle), and the unload force or contractive power as measured from the last retraction cycle at various elongations. Generally, five specimens were tested for each sample, with mean values over these samples developed.

For the films of the present invention, the preferred hysteresis properties which are obtained are as follows:

5 Permanent set (%) (obtained through use of a
modification of ASTM D-1682 wherein the stretching is
cycled rather than continued through film failure)
(150% extension, one cycle, MD): preferably less than
40, more preferably in the range of about 5 to about
10 25, most preferably less than 10-20; and/or

 Permanent set (%) (150% extension, 1 cycle, TD):
preferably less than 40%, more preferably in the range
of about 5 to about 25, most preferably less than 10-
15 20% and/or;

 Permanent set (%) (200% extension, 1 cycle, MD):
preferably less than 45%, more preferably in the range
of about 5 to about 25%, most preferably 5-15%; and/or
20

 Permanent set (%) (200% extension, one cycle, TD):
preferably less than 45%, more preferably in the range
of about 5 to about 25%, most preferably in the range
of about 5-15%; and/or
25

 Permanent set (%) (300% extension, 1 cycle, MD):
preferably less than 50%, more preferably in the range
of about 20 to about 40%, most preferably 15-30%;
and/or
30

 Permanent set (%) (300% extension, one cycle, TD):
preferably less than 50%, more preferably in the range
of about 20 to about 40%, most preferably in the range
of about 15-30%; and/or
35

Table 4 lists comparative data for the following
Examples 1-5 with Example 1 being the control using the

standard blend formulations. These examples were dry blended, then extruded on a 1 1/2" Egan blown film lab line. Melt strength, film appearance, and openability, were measured on line. Hysteresis testing was preferred at 200% extension in order to compare improvements to elastic recoverability.

EXAMPLE 1

Blend Formulation:

	<u>Component</u>	<u>Percentage</u>
10	KRATON D 2104	63%
	LD 767.36	27%
	MBX - 6	10%

15 The material extruded satisfactorily with good melt strength as indicated by the observed bubble stability. The collapsed film was peeled with no sticking or fusing, thereby qualitatively determining "openability" as good and given an "A" rating (based on an A, B, C, D scale with "A" being good and "D" being poor). The film appearance rating (FAR) was slightly grainy and qualitatively given a "B" rating based a scale which qualifies a totally clear film as an "A" rating while an opaque film would be rendered a "D".

20 This film is the "control" and will be used as the comparison hereinafter.

EXAMPLE 2

	<u>Blend Component</u>	<u>Percentage</u>
30	KRATON D 2104	63%
	XS 12.04	27%
	Ethyl Methyl Acrylate ("EMA")	
	MBX - 6	10%

35 The film produced had a less grainy appearance and rated a FAR of "B". Openability was slightly less than Example 1 and rated a "B" to "C". Elastic recoverability was slightly improved over the control.

The MD tensile set was 20% vs 22.6% (13% improvement) while the TD had a 17% improvement (18% vs. 21.2%).

EXAMPLE 3

5	<u>Component</u>	<u>Percentage</u>
	KRATON D 2104	63%
	TAFMER P0480	27%
	MBX - 6	10

10 The material processed well with observed excellent bubble stability and received a FAR rating of "A". The openability was slightly less ("B") than the control but tensile set was substantially improved. The MD set was 14.1% vs. 22.6% (60% improvement) while
15 the TD set displayed a 35% improvement (15.7% vs. 21.2%).

EXAMPLE 4

	<u>Component</u>	<u>Percentage</u>
20	KRATON D 2104	63%
	TAFMER P0280	27%
	MBX - 6	10%

25 Good extrusion performance with an excellent FAR rating of "A" and comparable openability to the control thereby deserving of an "A" rating. Again the tensile set properties were substantially improved over the control. The MD permanent set had an improvement of 50% (15.1% vs. 22.6%) while the TD had an improvement
30 of 39% (15.3% vs. 21.2%).

EXAMPLE 5

	<u>Component</u>	<u>Percentage</u>
	KRATON D 2104	63%
35	TAFMER P0180	27%
	MBX - 6	10%

The material was very splitting and broke upon extension in the TD. The FAR rated a "C" and openability rated a "B". The tensile set could not be measured in the TD but the MD had a 53% improvement over the control (14.8% vs. 22.6%).

The results of the first five examples are outlined in Table IV. Example 2 utilized EMA as a polyolefin component of the elastomeric blend to illustrate the use of another known component commonly cited, but not commercially preferable, for use in elastomeric blends. The overall conclusions reached for those specific embodiments of the invention in Examples 3-5 are that substantial improvements to tensile set (elastic recoverability) can be achieved by replacing the EVA component of the standard commercial blend as taught in prior art U. S. Patent 4,476,180, with a LLDPE plastomer copolymer such as the TAFMER P0480 and P0280 copolymers of Mitsui Corporation of Japan. As much as a 60% improvement has been demonstrated for tensile set (recoverability) over the control while maintaining comparable modulus and extrusion process performance in the preparation of the films as illustrated in the data of Table IV. Note that the recoverability of the film of Example 2 utilizing EMA demonstrated a tensile set which improved slightly over the EVA control, but was not as impressive as Examples 3-5 utilizing the LLDPE's of the present invention.

TABLE IV

HYSTERESIS RESULTS @ 200% EXTENSION

SAMPLE ID	BUR	DIE GAP (MIL)	YAG (MIL)	MODULUS		% TENSILE SET		UNLOAD FORCE (G)		
				(1) (G)	(2) (G)	(1) (%)	(2) (%)	25%	50%	200%
001 (CONTROL) KRATON D2104, SBC MD 28% EVA TD	2.1	35	2.05	313 216	270 193	18.7 17.4	22.6 21.2	-- --	21.2 17.9	227 164
002 (CONTROL) KRATON D2104, SBC MD 28% EMA TD	2.1	35	2.37	361 215	311 196	17.7 15.3	20.0 18.1	-- --	29.7 17.7	262 162
003 KRATON D2104, SBC MD 28% TAFMER P0480 TD	2.1	35	2.40	308 215	257 193	12.1 13.8	14.1 15.7	12.1 --	49.3 33.3	228 169
004 KRATON D2104, SBC MD 28% TAFMER P0280 TD	2.1	35	2.32	256 166	214 145	13.1 12.5	15.1 15.3	5.1 2.3	36.7 26.8	189 122
005 KRATON D2104, SBC MD 28% TAFMER P0480 TD	2.1	35	2.19	203 Broke	164 Broke	12.5 Broke	14.8 Broke	6.7 Broke	28.7 Broke	147 Broke

The following Table V lists comparative hysteresis data for Examples 6 through 11 at 150% extension. All samples were hot melt compounded on a 57 mm Zsk twin screw extruder described previously. Compounds were then run on a 1 1/2" Egan blown film line using both a 35 and 50 mil die gap. Film appearance, openability and bubble stability were measured qualitatively on line. Hysteresis testing was performed at 150% extension per the previously described method herein in order to compare improvements to elastic recoverability and any improvements to the process.

Comparisons were made with comparable die gaps. Therefore, Example 8 demonstrates a 22% improvement to tensile set over the control in Example 6 using the same amount of LLDPE (28%). Example 9 demonstrates comparable modulus and tensile set to the control of Example 6 using elevated amounts of LLDPE (48%). Similar results are obtained when comparing Example 7 with Examples 10 and 11.

TABLE V

HYSTERESIS RESULTS @ 150% EXTENSION

SAMPLE ID	BUR	DIE GAP (MIL)	YAG (MIL)	MODULUS (1) (G)	MODULUS (2) (G)	% TENSILE SET (1) (%)	% TENSILE SET (2) (%)	UNLOAD FORCE (g) 25%	UNLOAD FORCE (g) 50%	MI (DG/MIN)	DENSI. (g/cm ³)
006 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	35	2.19	304 286	262 265	---	11.1 10.3	---	---	4.4	.949
007 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	50	2.89	554 289	479 265	11.2 12.5	13.2 14.4	37 21	109 67	4.1	.941
008 KRATON D2104, SBC 28% EXXPOL	2.1	35	2.31	292 362	267 330	---	9.13 8.57	---	---	---	---
009 KRATON D2104, SBC 48% EXXPOL	2.1	35	2.25	309 342	278 317	---	12.9 12.6	---	---	3.1	.926
0010 VECTOR 7400D, SBC 28% EXXPOL	2.2	50	2.68	480 244	412 224	8.5 11.1	10.5 13.1	74 39	145 82	2.8	.920
0011 VECTOR 7400D, SBC 48% EXXPOL	2.2	50	2.63	451 368	398 330	11.1 12.5	13.1 14.4	36 18	109 85	2.7	.916

EXAMPLES 6 & 7 (Controls)

	<u>Component</u>	<u>Percentage</u>
	KRATON D 2104	63.7%
	LD 767.36	28.8%
5	Spectrathene	
	(CM 19002)	7.0%
	Euracamide	.3%
	IR 1076	.2%

10 The Example 6 fabrication of the controls for the
150% hysteresis testing in Table V was performed using
a 35 mil die gap while Example 7 used a 50 mil gap.
Both had good bubble stability and FAR "A". The film
appearance was improved over dry blends of Example 1 in
15 that they displayed no grainy appearance. Openability
was good but did display some blocking ("B" rating).
Permanent set was somewhat better using the 35 mil die
gap for Example 6 vs. 50 mil gap for Example 7. Also
the MD modulus was higher for Example 7 vs. 6, but TD
20 modulus was comparable.

EXAMPLE 8

	<u>Component</u>	<u>Percentage</u>
	KRATON D 2104	63.7%
25	EXXPOL WS-9905	28.8%
	Spectrathene	
	(CM 19002)	7.0%
	Euracamide	.3%
	IR 1076	.2%

30 Film appearance (FAR "A") and bubble stability
were excellent. Film openability was substantially
superior to the control and given an "A+" but the motor
load and pressure were higher. MD tensile set was 22%
35 improved (9.13% vs. 11.1%) over the control Example 6
(Control). An unexpected finding was the improvement
to openability using the EXXPOL polymer as a
replacement to the commercially accepted EVA. This use

of the EXXPOL LLDPE in place of the standard EVA will not only improve the processability, but will allow reduced slip levels, thus saving additive costs and downtime for downstream converters due to slip build up.

EXAMPLE 9

	<u>Component</u>	<u>Percentage</u>
	KRATON D 2104	46.25%
10	EXXPOL WS-9905	46.25%
	Spectrathene	
	(CM 19002)	7.0%
	Euracamide	.3%
	IR 1076	.2%

15

Again bubble stability and FAR were excellent ("A" FAR rating) and openability was significantly improved over the controls and earned an "A++". Tensile set and modulus were comparable to the control of Example 6 at 20 35 mil die gap. The advantage over the Example 6 control is the reduced amount of slip agent and SBC component, thus reducing cost of fabricating the film.

EXAMPLE 10

	<u>Component</u>	<u>Percentage</u>
25	VECTOR 7400D	63.7%
	EXXPOL W5-9905	28.8%
	Spectrathene	
	(CM 19002)	7.0%
30	Euracamide	.3%
	IR 1076	.2%

This compound was compared against the Example 7 Control using the 50 mil die gap. Bubble stability and 35 FAR were excellent ("A"). Film openability was significantly better than all other blends when the EXXPOL SSC and VECTOR SBC from the Dexco Company were compounded together and rated an A+++. Also the

modulus and tensile set of this particular blend were substantially improved over the control (16% and 26% respectively) while the unload force (contractive power) was comparable to the commercially satisfactory controls. The unexpected finding was the improved openability for the VECTOR SBC EXXPOL's blend compared with the controls employing the same additive package.

EXAMPLE 11

10	<u>Component</u>	<u>Percentage</u>
	VECTOR 7400D	46.25%
	EXXPOL WS-9905	46.25%
	Spectrathene (CM 19002)	7.0%
	Euracamide	.3%
15	IR 1076	.2%

Film processability was comparable to the control (Example 7) but had somewhat higher load and pressure. The openability was comparable to Example 10 and substantially better than the EVA/KRATON blends. Modulus and tensile set were also comparable to the control showing that comparable properties can be achieved versus the control but at reduced SBC and slip additive levels which will substantially reduce costs and save downtime for convertors using embodiments of this invention.

EXAMPLE 12

COMPONENT	PERCENTAGE
VECTOR 7400D	60%
LD 767.36	32.1%
CM 19002	7%
EURACAMIDE	.7%
IR 1076	.2%

EXAMPLE 13

COMPONENT	PERCENTAGE
VECTOR 7400 D	60%
EXACT 4049	32.6%
CM 19002	7%
EURACAMIDE	.2%
IR 1070	.2%

5 In both Examples 12 and 13, samples were produced on a commercial blown film line. The samples were tested at 300% extension in the traverse direction.

10 In Table VI, the results of the comparative hysteresis data are listed. As shown, the tensile set of Example 13 (Exxpol Plastomer) was 22% compared to the 38% for the sample of 12 (EVA) demonstrating a 72% improvement in the tensile set of the SBS/Exxpol plastomer film.

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TABLE VI

Hysteresis Results @ 300% Extension (TD)

SAMPLE ID	YAG MIL	MODULUS GRAMS	%TENSILE SET (%)
012 Vector 7400D EVA	2.664	545	38
013 Vector 7400D Exact 4049	2.651	323	22

The overall conclusions reached for these specific embodiments of the invention are that improvements to openability can be achieved by replacing the EVA with SSC EXXPOL plastomers. Also, substantial improvements to tensile set (elastic recoverability) can be achieved by replacing the KRATON SBC from Shell with the VECTOR 7400D SBC from Dexco. Ideally, the overall improvements afforded with the EXXPOL and Dexco VECTOR SBC used in combination not only improve tensile set, but processability as well. The improved openability afforded by these blends will not only reduce costs because of unnecessary additives (slip agents) but reduction in the amount of the SBC component as well. This particular embodiment will prove beneficial to convertors who use film produced from this invention in that reduced slip levels will equate to longer run time due to reduced slowdowns caused by slip buildup.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the invention. The appended claims are intended to cover all such modifications that are within the scope of this invention.

IN THE CLAIMS

What is claimed is:

- 5 1. A thermoplastic elastomeric film comprising:
 - a. a monoalkenyl arene-diene elastomeric block copolymer; and
 - 10 b. A copolymer of ethylene and at least one comonomer, the polymer having a density in the range of about 0.86 to about 0.900 g/cm³, a MWD in the range of about 2 to about 3.5, a melt index in the range of about .2 dg/min to
15 about 1000 dg/min, and an ethylene crystallinity less than 35%.
2. The film of claim 1 wherein the comonomer of the ethylene copolymer comprises ethylenically
20 unsaturated olefin(s) having from 3 to about 20 carbon atoms.
3. The film of claim 2 wherein the comonomer comprises one or more of propylene, butene-1,
25 hexene-1, octene-1, 4-methyl-1-pentene, and styrene.
4. The film of claim 1 wherein the copolymer has a density in the range of about 0.86 to about 0.90
30 g/cm³.
5. The film of claim 1 wherein copolymer MWD is in the range of about 2.0 to about 3.5.
- 35 6. The film of claim 1 wherein the polyethylene copolymer has a CDBI greater than 45%.

7. The film of claim 1 wherein the elastomeric block copolymer is styrene-butadiene copolymer having a styrenic content of from 8-55% of the block copolymer.
- 5 8. The film of claim 1 wherein the elastomeric block copolymer is present in amounts of between about 45% to 65% by weight.
- 10 9. The film of claim 1 wherein the ethylene copolymer is present in amounts of between 20 to 60% by weight.
- 15 10. The film of claim 1 wherein the elastomeric copolymer is present in amounts of between about 45 to 65% by weight and the ethylene copolymer is present in amounts of between 25 to 50% by weight.
- 20 11. The film of claim 1 wherein the elastomeric block copolymer is a styrene-isoprene copolymer.
12. The film of claim 1 in which the tensile set, after one cycle of 150% extension in the machine or traverse direction, is below 30%.
- 25 13. The film of claim 1 in which the tensile set, after one cycle of 150% extension in the machine or traverse direction, is between 5-15%.
- 30 14. The film of claim 1 having a tensile set, after one cycle of 300% extension in the traverse direction, of less than about 40%.
- 35 15. The film of claim 19 in which the tensile set is less than about 20%.

16. The film of claim 1 having a tensile set, after one cycle of 200% extension in the machine or transverse direction, is between 5-15%
- 5 17. The film of claim 1 having:
- (a) a tensile set, after one cycle of 150% extension in the machine or traverse direction of less than about 20%;
 - 10 (b) a tensile set, after one cycle of 200% extension in the transverse direction of less than about 25%; and
 - 15 (c) a tensile set, after one cycle of 300% extension in the transverse direction of less than about 40%.
18. A method for producing an elastic film, said method comprising the steps:
- 20 (a) providing the LLDPE plastomeric styrenic block copolymer/elastomer film blend of claim 1.
 - 25 (b) converting said plastomer/elastomeric block copolymer blend into a film by a film making process of slit-die extrusion, cast die extrusion, cast/embossed extrusion processing
 - 30 or by melt blowing said plastomer.
19. The method of claim 18 wherein the film conversion is a die castings process comprising:
- 35 (a) extruding the blend composition through a die having a gap greater than about 5 mils and less than 20 mils;

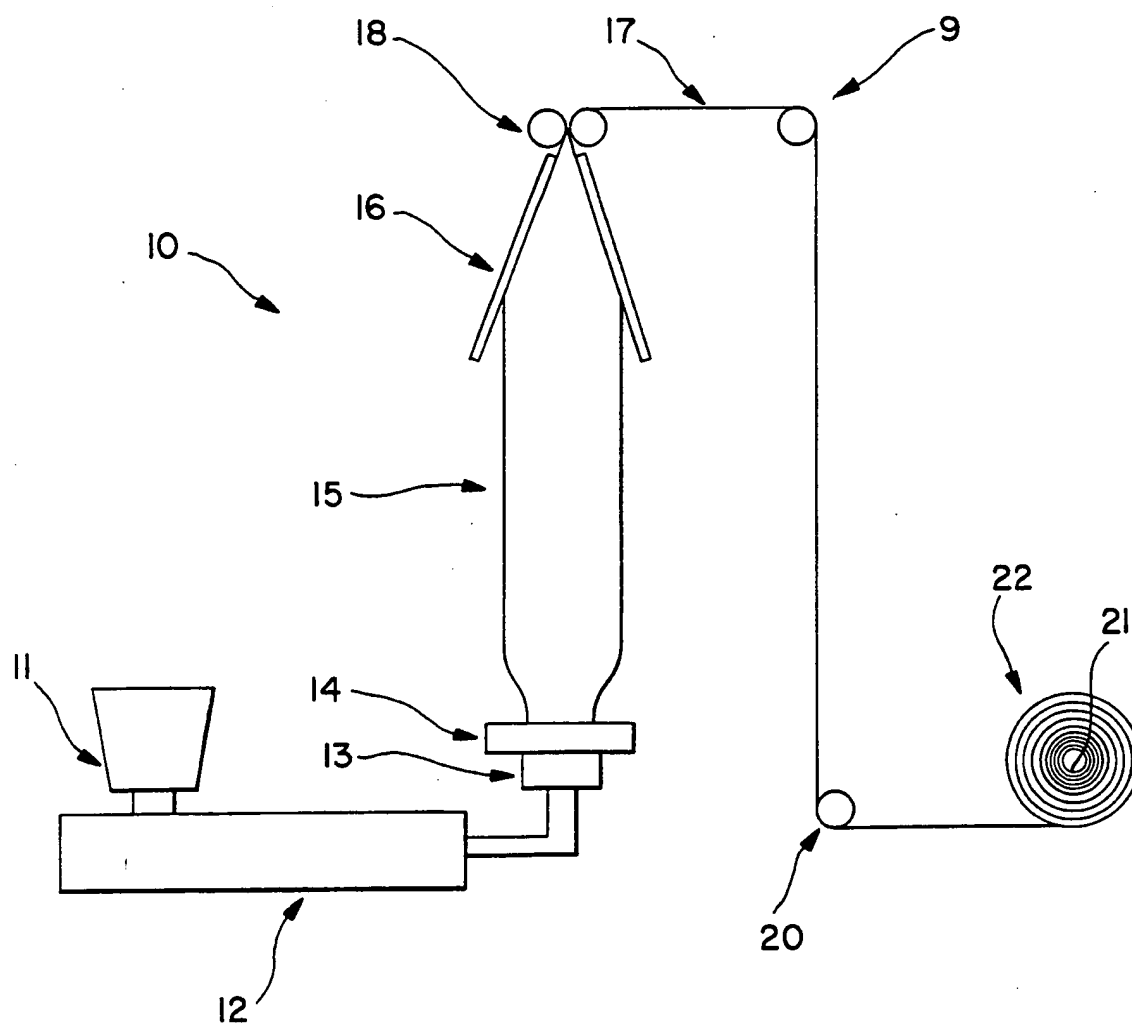
(b) expanding the extruded film to a thickness of between 0.5 mils and about 15 mils; and

5 (c) rapidly cooling the expanded film.

20. The method of claim 18 wherein said film is oriented to a total draw down ratio in the range of about 2:1 to about 100:1 through a blown film
10 or cast film die.

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FIG. 1



INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 94/01376

A. CLASSIFICATION OF SUBJECT MATTER IPC 5 C08J5/18 B29D7/01 C08L23/08 //B29K9:06, B29K23:00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 5 C08J B29D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 7944, Derwent Publications Ltd., London, GB; AN 79-79624B & JP,A,54 120 646 (DENKI KAGAKU KOGYO) 19 September 1979 cited in the application see abstract ---	1-4, 7-11, 18-20
X	EP,A,0 114 964 (MILES LABORATORIES) 8 August 1984 see page 3, line 13 - page 4, line 5; examples 1-3 --- -/--	1-4, 7-11, 18-20
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 25 May 1994		Date of mailing of the international search report 27 -06- 1994
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Attalla, G

INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/US 94/01376

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>GB,A,2 178 433 (KIMBERLY-CLARK) 11 February 1987</p> <p>see page 8, line 15 - line 35; example 32</p> <p>-----</p>	<p>1-4, 7-11, 18-20</p>

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